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Properties of Aqueous Solution of Polyoxyethylene mono-alkyl Ether

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INTRODUCTION

Ionic surfactants in their aqueous solution are characterized by a high degree of association into colloidal micelles above a certain concentration, the so-called critical micelle concentration (c.m.c.)[1]. Since association in solution of those surfactants is attributable to the contradictory solubility relation exhibited by the polar and nonpolar groups within the molecules, Gonick and McBain[2] expected non-ionic surfactants to exhibit colligative properties similar to those of the ionic type, and they showed for the first time that non-ionic surfactants of ester type (nonaethylene glycol monolaurate, Detergent "X" and Triton X-100) form colloidal micelles principally by means of cryoscopic evidence.

In the present report, various properties of the aqueous solutions of non-ionic surfactants in ether type are discribed and discussed with respct to their micelle formation.

EXPERIMENTAL

Materials : Surfactants used in the present work are principally polyoxyethylene glycol alkyl ethers, $HO(C_2H_4O)_n(CH_2)_mH$, and those used in the previous experiment[3]. In the notation of the kinds of samples, lauryl, oleyl and cetyl are abbreviated to L, O and C respectivery, and figures represent the degree of polymerization of polyoxyethylene. For the standard sample, pure hexaoxyethylene glycol lauryl ether (abbreviated to PL-6) was prepared in the authors' laboratory. Most of the experiments were carried out at room temperature.

RESULTS AND DISCUSSION

1. Density

Densities of the aqueous solutions were measured with the Ostwald's type picnometer (*ca.* 30 cc) at 25℃. As shown in Fig. 1, the density of the L-6 solution remains almost constant until the concentration comes to a certain value and then increases gradually with the concentration. In Fig. 1, also the partial specific volumes are plotted against concentration. The partial specific volume V were calculated by the following relation :

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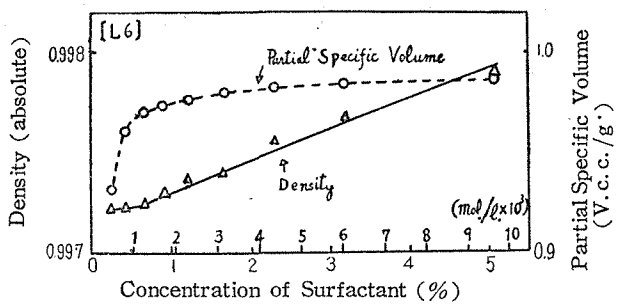

Fig. 1. Variation of density and partial specific volume with concentration in aqueous surfactant solution.

$$V = \frac{1}{h}\left(\frac{w}{\rho} - \frac{s-h}{\rho}\right),$$

where h is the weight of the dry surfactant in the picnometer, s the weight of the solution, w the weight of the solvent and ρ the density of the solvent. Comparing with the specific volume of L-6 (1.02 cc./g. at 25°C) in bulk state, the partial specific volume of the solute in the aqueous solution is considerably small at low concentrations and comes nearer to the value in bulk with increase of the concentration. Aqueous solutions of other surfactants gave similar results to L-6.

Such change in density against the concentration suggests that the surfactants in the solution vary their degree of dispersion with their concentration. It seems that phase separation proceeds in the solution gradually as the concentration increases. And the rate of change of the partial specific volume is relatively large at low concentration and becomes smaller above a certain concentration. Davies and Bury[4], and also Vetter[5] found similar facts in the aqueous solutions of ionic surfactants and defined the c.m.c. as the concentration at which the partial specific volume starts to increase. In comparison with the results obtained with respect to the ionic surfactants, it may be deduced that the increase in the partial specific volume of the non-ionic surfactants corresponds to the micelle fromation.

2. Viscosity

The relative viscosities η_r of the solution were measured with Ostwald's type viscometer at 31°C. As shown in Fig. 2., the increase of η_r becomes noticeable above the concentration of *ca.* 10^{-3} mole/1. The reduced viscosity η_{sp}/c are plotted against the concentration C in Fig. 3. The plots show generally that the reduced viscosities decrease with increase of the concentration, and some of them increase again above certain concentrations. Similar behavior has been observed with several colloidal- or poly-electrolytes. Kern[6] and Seiyama[7] ascribed the decrease of reduced viscosity to the characteristics of the electrolytes (ionic factor) and its increase to that of mac-

romolecules (macromolecular factor). Recently, Nakamura and Kubo[8] showed that the $\eta_{sp}/\sqrt{C}$ of pottasium chloride solution decreases linearly with $\sqrt{C}$ in accordance

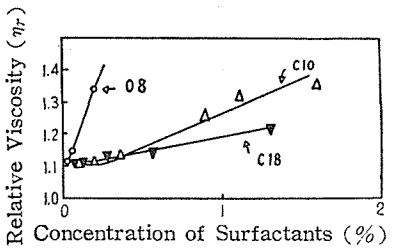

Fig. 2. Relation between relative viscosity and concentration of surfactants.

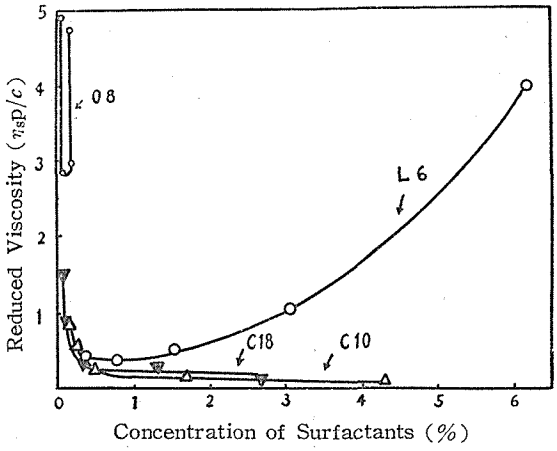

Fig. 3. Plots of reduced viscosity against concentration of surfactants.

with the theory of electrolytes of Falkenhagen. However, such decrease of the reduced viscosity has been observed not only with ionic substances but also with non-ionic substance. Sata and Tyuzyo[9] measured the diffusion constants and the reduced viscosities of ionic and non-ionic surfactants, and pointed out that the minimum point of reduced viscosity against the concentration corresponds to the c.m.c. of the solution. With respect to the reduced viscosity, similar facts has been observed also in organic solutions of surfactants by the present authors[10] and in organic solutions of polyvinyl chloride by Takeda and Tsuruta[11]. Comparing with the change of partial specific volume mentioned above, the decrease of the reduced viscosity of surfactants with the concentration may be closely related with micelle formation in the solution. As to the characteristic behavior of viscosity in the aqueous solution of surfactants, there are problems to be discussed further, as Fuoss[12], and Rosen, Kamath and Eirich[13] have shown.

3. Absorption Spectrum of Dye Solution

Pinacyanol chloride is tinged with purple in its aqueous solution and with blue in its alcoholic solution. The aqueous solution of the dye changes its color above a certain critical concentration of the surfactant, where the solution shows similar tone of color with the alcoholic solution of the dye. This color change has been explained in terms of solubilization of the dye into the micelles of the surfactants.

Now, keeping pinacyanol chloride at a constant concentration (*ca.* 1×10^{-5} mole/l),

changes of absorption spectrum of the dye solution against the concentration of the surfactants were observed with Beckman's spectrophotometer. It was found that the absorption spectrum of the dye solution containing the non-ionic surfactant showed two characteristic absorption bands, α (600mμ) and β (550mμ) bands as shown in Fig. 4 and Fig. 5, while in the case of anionic surfactant, sodium lauryl sulfate (S.L.S.), γ band appeared at low concentration range, and above a certain concentration, α and β bands appeared instead of γ bands. Change of instensities of α, β and

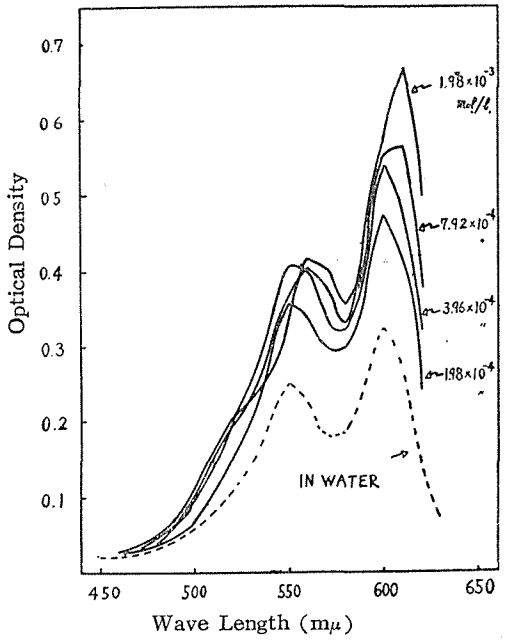

Fig. 4. Absorption spectrum of aqueous solution of pinacyanol chloride as a function of concentration of non-ionic surfactant (PL6).

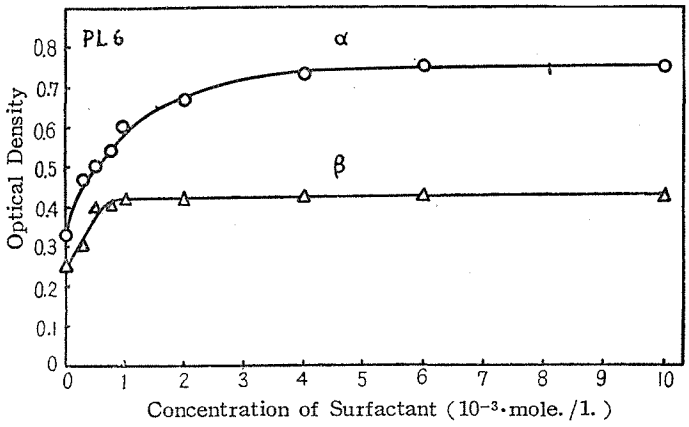

Fig. 5. Relation between concentration of non-ionic surfactant (PL6) and optical density of two characteristic bands.

γ bands in the case of anionic surfactant, are plotted against the concentration of the

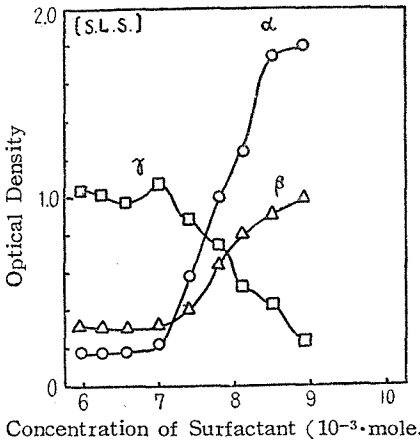

Fig. 6. Relation between concentration of anionic surfactant (S.L.S.) and optical density of three characteristic bands.

surfactant in Fig. 6. It seems that at low concentration rang of the anionic surfactant, α and β bands are suppressed by γ band. According to the experiment of Klevens[14], the medial value of the concentration at which α band rises, corresponds with the so-called c.m.c. Comparing with the results of the ionic surfactant, the c.m.c. of the non-ionic surfactants PL-6, falls at a concentration of about 10^{-4} mole/1 whose magintude is in the same order of magnitude with the results of Gonick and McBain obtained with the non-ionic surfactants in ester type. Other non-ionic surfactants showed similar results with PL-6.

γ band at low concentration of the anionic surfactant may be ascribed to the ionic interaction between the dye and the surfactant. Concerning the change of α and β band above the c.m.c., there seems to be no essential difference between ionic and non-ionic surfactants. From this fact, it is suggested that the micelle formation itself is not affected essentially by the ionic character of the surfactants as Philipoff[15] pointed out, but rather it may be dependent upon the surfactant molecules.

4. Solubilization of Sudan III

The dyestuff Sudan III is almost insoluble in water but soluble in alcohol. Alcoholic solution of this dye is tinged with red orange and its characteristic absorption is shown at 490 mμ. Now, change of intensity of the characteristic absorption due to Sudan III was observed with the aqueous solution of non-ionic or ionic surfactants at various concentrations. The results are shown in Fig. 7. In the case of anionic surfactant, sodium lauryl sulfate (S.L.S.), solubilization of Sudan III was recognized above *ca.* 6×10^{-3} mole/1. which is somewhat lower than the c.m.c. obtained by another method. For the non-ionic surfactant, PL-6, it was found that solubilization occurs at

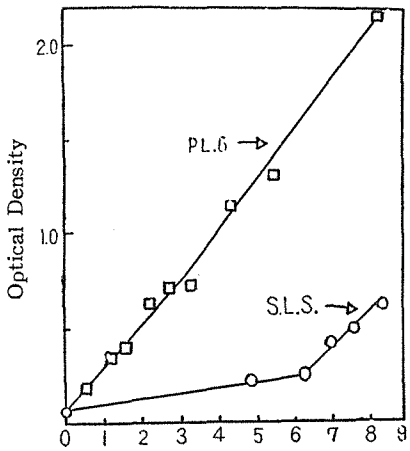

Fig. 7, Comparison of solubilization curves for non-ionic and anionic surfactant.

concentration range far lower than in the case of the ionic surfactant. In comparison with other experimental results shown above, such solubilization may be ascribed to micelle formation of the non-ionic surfactant in the solution, though the c.m.c. was not determined accurately.

SUMMARY

Concerning the aqueous solutions of non-ionic surfactants, it was observed that partial specific volume, reduced viscosity and solubilization of dyes against their concentrations showed relatively large rate of change at low concentration range (*ca.* 10^{-4} mole/1.) and such behaviours were ascribed to the micelle formation in the solution in comparison with the case of ionic surfactants, though their c.m.c. were not detemined accurately. And it was suggested that the micelle formation is not necessarily dependent upon the ionic character of the surfactants but upon the polar and non-polar constitution of the surfactant molecules by the reason that the micelle formation can be recognized not only in the aqueous solution of non-ionic surfactants but also in the organic solution of surfactants as reported by Askin and Singleterry[16] or others[15].

ACKNOWLEDGEMENTS

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